

DE 14 44 275

AMENDED SPECIFICATION

Reprinted following proceedings under Sections 17(1) and 14 of the Patents Act, 1949, allowed on the 16 March 1967 and 7 March 1968, respectively.

PATENT SPECIFICATION

L060.734



NO DRAWINGS

L060.734

Date of Application and filing Complete Specification: Dec. 13, 1963.  
No. 49312/63.

Application made in Switzerland (No. 14667) on Dec. 13, 1962.

Application made in Switzerland (No. 13389) on Oct. 31, 1963.

Complete Specification Published: March 8, 1967.

© Crown Copyright 1967.

Index at acceptance:—D1 B(2C1A8, 2M)

Int. Cl.:—D 06 p

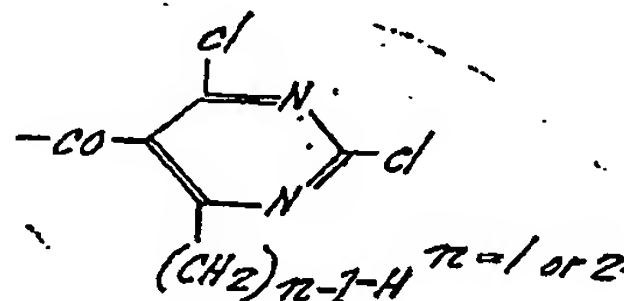
The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are:—MIRO CAPPONI of Neubadstrasse 150, Basle, Switzerland and EMIL METZGER of Niederholzboden 44, Riehen, Switzerland, both Swiss Citizens.

COMPLETE SPECIFICATION

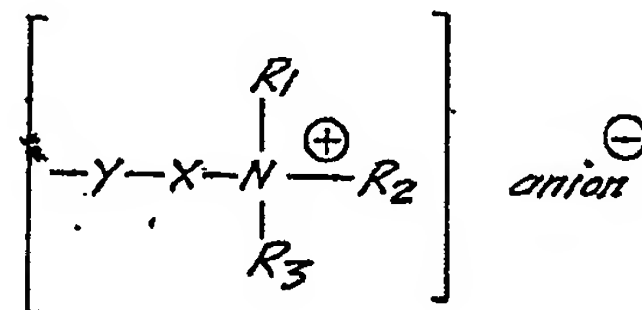
Dyeing and Printing with Reactive Dyes

We, WESTMINSTER BANK LIMITED, of 41, Lothbury, London, E.C.2, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the dyeing and printing of cellulosic textile materials with reactive dyes, which are applied at 15—40°C and fixed at 15—40°C in an alkaline medium. The process consists in the use of a reactive dye of moderate substantivity which contains a dichloropyrimidyl-5-carbonyl-group of the formula

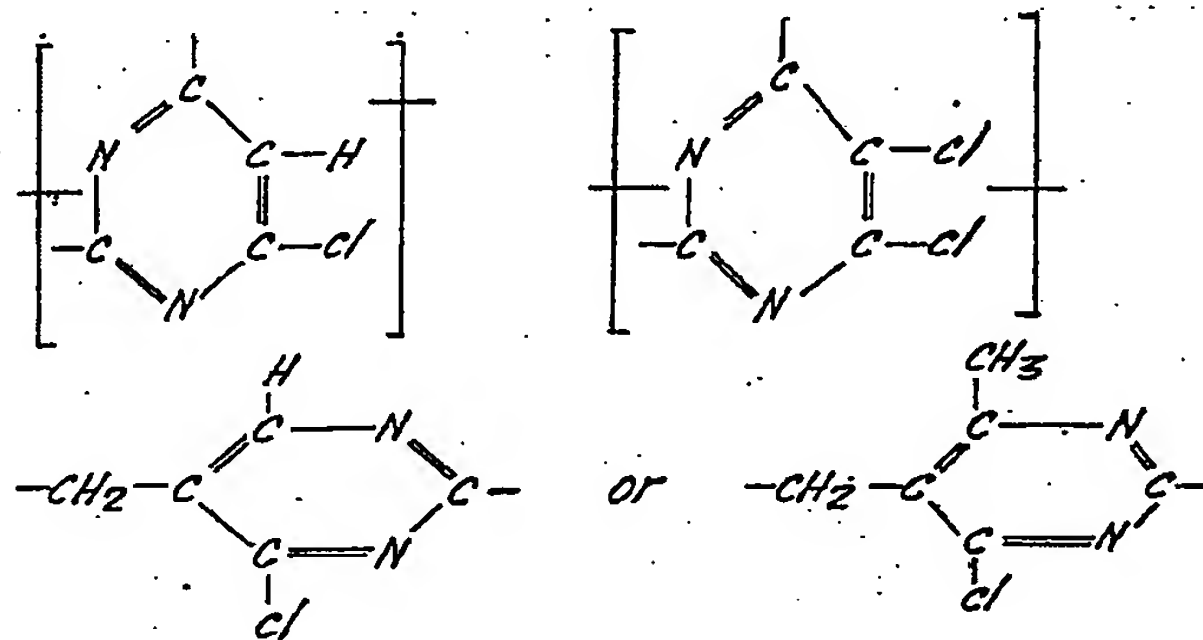


or a radical of the formula



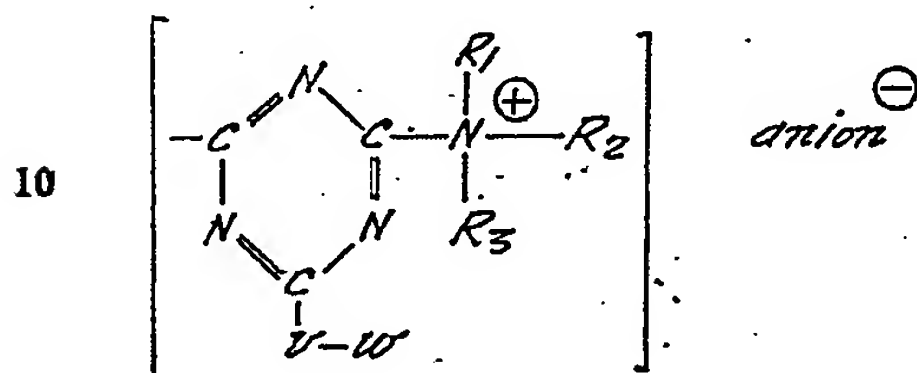
wherein X represents a halogen-substituted bridge member of the 1,3-diazine series, e.g.

[Price 4s. 6d.]



Y represents an oxygen atom or an imino group, which may be alkylated, R, represents —NH<sub>2</sub>, and

- 5 R<sub>2</sub> and R<sub>3</sub> each represent methyl or R<sub>2</sub> and R<sub>3</sub> together with N from a pyrrolidyl or piperidyl radical (when Y represents an oxygen atom the quaternation can be effected in the fixing both itself) or a radical of the formula



wherein

v represents an oxygen or sulphur atom or a substituted or unsubstituted imino group, w represents hydrogen or a substituted or unsubstituted alkyl, aralkyl, cycloalkyl or aryl radical, and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> have the meanings ascribed to them above, being a reactive dye whose content of hydrolysis rate at the fixing temperature and at a pH value of 10.5 is greater than 5 × 10<sup>-3</sup> min.<sup>-1</sup> and carrying out the fixation in the pH range of from 8 to 14.

As reactive dyes of moderate substantivity are understood dyes which in 60 minutes in the presence of 30 grams of sodium chloride per liter have a drawing capacity of at least 20% on mercerised cotton, the temperature being 50°C and the liquor ratio 1:30; the drawing capacity is determined with a dye solution which, diluted 1:25, has an optical density of 0.5 at a layer thickness of 10mm, the measurement being made colorimetrically at the absorption maximum.

The cellulosic textiles which can be dyed or printed by the process may be filaments, loose fibres or woven or knitted fabrics of natural cellulose, e.g. of cotton, mercerised cotton or linen, or of regenerated cellulose, e.g. viscose filament or staple fibre, cuprammonium rayon, or blended yarns or fabrics or other articles composed of one of the aforementioned fibres

and a natural or synthetic polyamide fibre, e.g. wool, silk, nylon, or a polyester or acrylic fibre. After the application of the padding liquor or printing paste, the goods can be dried before fixation, if desired.

Fixation of the applied padding liquor or printing paste is accomplished in 5—60 seconds, or preferably 5—10 seconds, and preferably it is carried out continuously, for instance on roller vats, chemical pads, or similar equipment with provision for impregnation and expression of the fixing liquor. The dyeing and printing of the aforementioned textile materials can be carried out by the conventional methods. The fixation liquor is adjusted to a pH value of 8—14, or preferably 8.5—12.5.

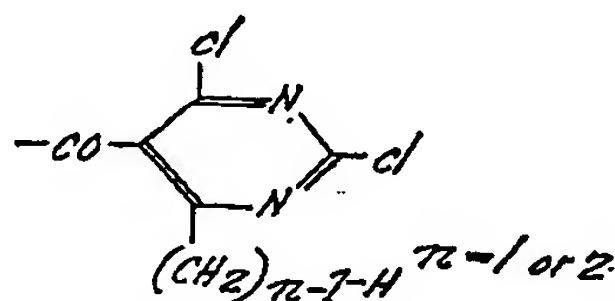
The fixation liquor contains a compound or a mixture of compounds or alkaline reaction, e.g. sodium metasilicate, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, sodium or potassium silicate in which the molecular ratio of SiO<sub>2</sub>:Na<sub>2</sub>O or K<sub>2</sub>O is 2—3.5:1, or preferably 3.3:1, so-called sodium water glass. It is advisable to introduce an air passage of 2 seconds to 2 minutes after padding and before and/or after fixation. The process is suitable for producing dyeings and prints in all depths. For example, a printing paste may contain 0.01 to 100 parts of dye per 1000 parts of the paste, or preferably 5 to 40 parts per 1000 parts paste. The commonly used printing assistants and other agents can be added to the pastes, for example, solvents (such as urea, thiodiethylene glycol, butyl carbitol and glycerine), thickening agents, fluorescent brightening agents, levelling agents, and wetting agents. Suitable thickening agents are gum tragacanth, locust bean gum and its derivatives, sodium alginates, starch and starch derivatives. The padding liquors also can contain the standard assistants, for example wetting and levelling agents. The padding liquors can be prepared with 1—100 parts, or preferably 10—50 parts of dye for 1000 parts of the liquor. The textile material is padded and expressed to a pick-up of 40—180%, or preferably 60—80%. With the new process bright, deep dyeings

and prints can be produced on the above-mentioned substrates which are outstandingly fast to wet treatments such as washing, perspiration, water, sea water, alkali, scrooping, and to gas fumes, rubbing, sublimation, pleating, pressing, decatizing and solvents. The light fastness too is very good.

These good wet fastness properties are due to the formation of a stable chemical linkage between the dye molecule and the cellulose molecule. Often the entire amount of dye applied does not take part in the chemical reaction with the substrate, and the proportion of unfixed dye is then removed by suitable operations such as rinsing and/or soaping, if necessary at high temperatures, for which purpose synthetic detergents may be used, such as alkylaryl-sulphonates, e.g. sodium dodecylbenzene-sulphonate, alkyl sulfates, e.g. sodium lauryl-, cetyl- or oleyl-sulphate, alkylpolyglycol ethers, and mono- or di-alkylphenylpolyglycol ethers which may be sulphated or carboxymethylated, e.g. sodium laurylpolyglycol ether sulphates. The textile material can alternatively be padded or printed with an acid or neutral padding liquor or printing paste, and then expressed, dried if necessary, and overpadded with a liquor of alkaline reaction. The dye is then fixed at a pH value of 8–14, or preferably 8.5–12.5.

The fixing temperature is governed by the reactivity, i.e. the magnitude of the constant of the hydrolysis rate. Dyes having a high constant of hydrolysis rate at 20°C and pH 10.5 can be fixed at 15–25°C, while for dyes of lower hydrolysability, fixation must be carried out at temperatures of 30–40°C.

In the case of dyes of low hydrolysability containing a dichloropyrimidyl-5-carbonyl-group of the formula



instead of increasing the fixing temperature, a fixation catalyst of the formula



wherein  $R_4$  represents methyl or  $-NH_2$ , and  $R_5$  and  $R_6$  each represent methyl or  $R_3$

and  $R_6$  together with N form a pyrrolidyl or piperidyl radical, or

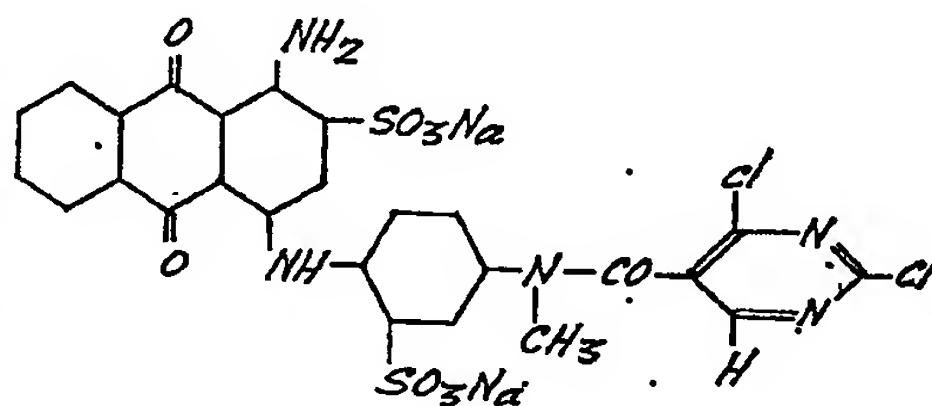
$R_4$ ,  $R_5$  and  $R_6$  together with N form the radical of triethylene-diamine, can be used, preferably in approximately equimolecular amounts. The chlorine atoms of such dyes react with catalysts of this formula to form a quaternary ammonium group having very high reactivity.

Suitable dyes belonging to the reactive class are, for instance, water-soluble, preferably metal-free, metallisable or metallised dyes of the mono-, dis- or poly-azo series, water-soluble dyes of the anthraquinone, pyrazolone, nitro, stilbene, di- or tri-arylmethane, azine, oxazine, thiazine, perinone, naphthoquinone, indigo, quinonaphthalone, xanthene, acridine, quinoline or phthalocyanine series.

In the following examples the parts and percentages are by weight and the temperatures in degrees centigrade.

#### EXAMPLE 1.

Mercerised cotton fabric is padded with a solution at room temperature containing, per 100 parts of water, 2 parts of the dye of the formula

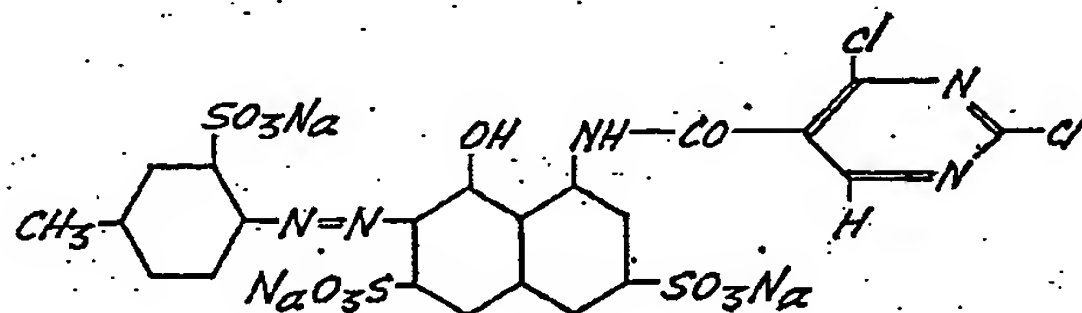


and the fabric expressed to a pick-up of 70%. The padding is continuously fixed in 30 seconds at 40° in a solution of 15 parts of anhydrous sodium sulphate and 0.2 part of sodium hydroxide in 100 parts of water contained in a roller vat, the solution having a pH of 11.85. The unfixed proportion of dye is then removed from the fabric by rinsing in cold and warm water followed by soaping at the boil. A reddish blue dyeing is obtained which has good light and wet fastness properties, e.g. good washing fastness.

When 1 part of sodium metasilicate is used in place of 0.2 part of sodium hydroxide, equally good results are obtained.

#### EXAMPLE 2.

Cotton fabric, previously bleached and treated with a sodium hydroxide solution is padded at room temperature with a solution containing per 100 parts of water 0.5 part of common salt and 2 parts of the dye of the formula



and expressed to contain 65% of its weight of the liquor. After intermediate drying the padding is continuously fixed in 30 seconds in a roller vat containing a solution of 20 parts of common salt and 0.2 part of sodium hydroxide in 100 parts of water at 40°, the pH of the solution being 11.55. The unfixed

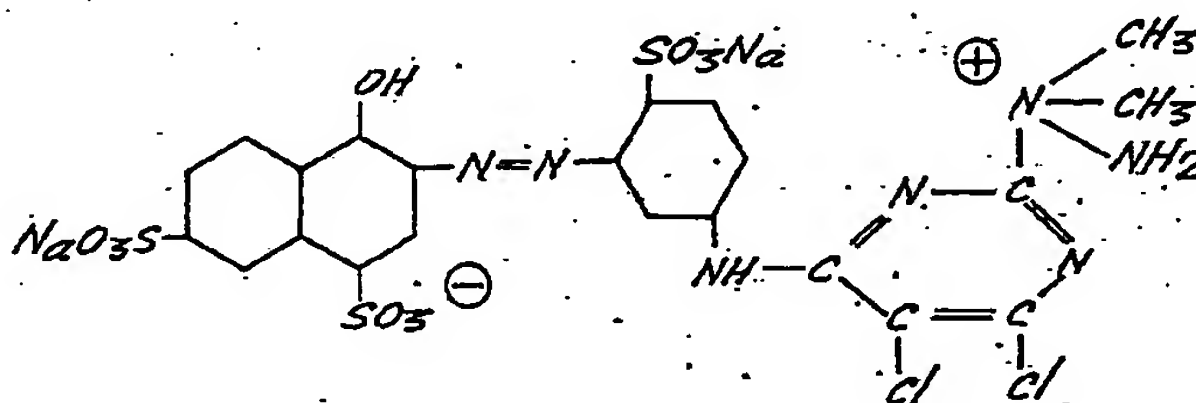
dye is removed by cold and warm rinsing and soaping at the boil. A red dyeing with good wet fastness properties is obtained.

Equally good results are obtained with the condensation products of 2,4-dichloropyrimidine- or 2,4-dichloro-6-methylpyrimidine-5-carbonylchloride and the following dyes:

		Shade
20	A 1-amino-4-(4'-aminophenylamino)-anthraquinone-2,3',5/8-trisulphonic acid	greenish blue
	B Copper phthalocyanine-3,3',3''-trisulphonic acid-3'''-sulphonic acid-(metaaminophenylamide)	turquoise
25	C 1:2-cobalt complex compound of 1-hydroxy-2-(2'-hydroxy-5'-nitrophenylazo)-6-aminonaphthalene-3,3'-disulphonic acid	brown
	D 1-(2',5'-dichlorophenyl)-3-methyl-4-(3''-aminophenylazo)-5-pyrazolone-4',6''-disulphonic acid	greenish yellow

### EXAMPLE 3.

Mercerised cotton fabric is padded at room temperature with a solution of 15 parts of urea and 2 parts of the dye of the formula



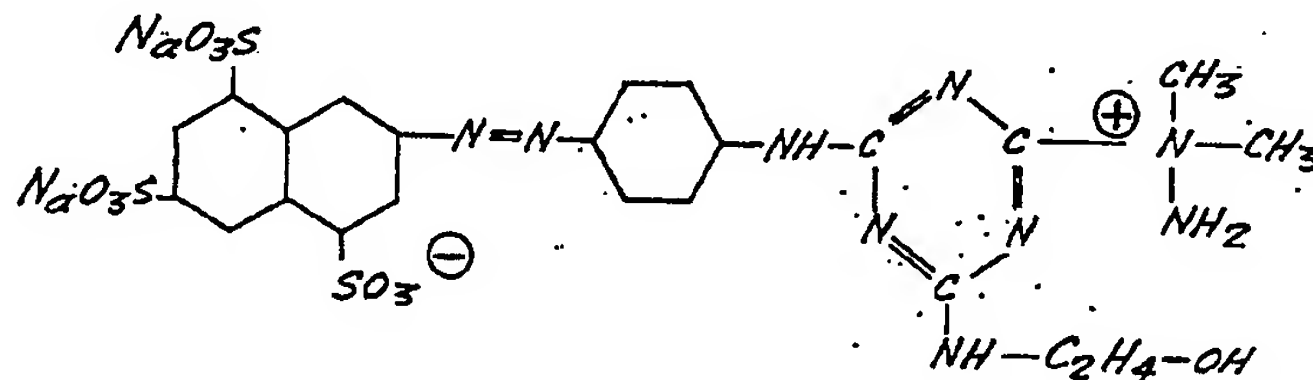
in 100 parts of water, and expressed to a pick-up of 80%. The padding is fixed in 30 seconds in a roller vat in a solution having a pH of 11.85 and containing 60 parts of calcined sodium sulphate and 2 parts of sodium hydroxide per litre water at 40°. The pro-

portion of unfixed dye is cleared from the fabric by rinsing in cold and warm water and subsequent soaping at the boil. The fabric is dyed to a scarlet shade which has good light and wet fastness properties, e.g. good wash fastness.

## EXAMPLE 4.

Mercerised cotton fabric is padded at 25° water 2 parts of the monoazo dye of the formula

5



and expressed to a pick-up of 70%. Fixation is effected by a passage of 15 seconds through a solution at 40° containing 150 parts of calcined sodium sulphate and 2 parts of sodium hydroxide per litre water, the pH of the solution being 11.85. The dyed goods are rinsed in cold and warm water, soaped for 15 minutes in a solution of 1 g/l sodium dodecyltriglycol ether sulphate and 1 g/l sodium carbonate at 95—100°, rinsed again and dried. A yellow dye fast to light and wet treatments is obtained.

Equally good results are obtained with dyes of the same general constitution which bear

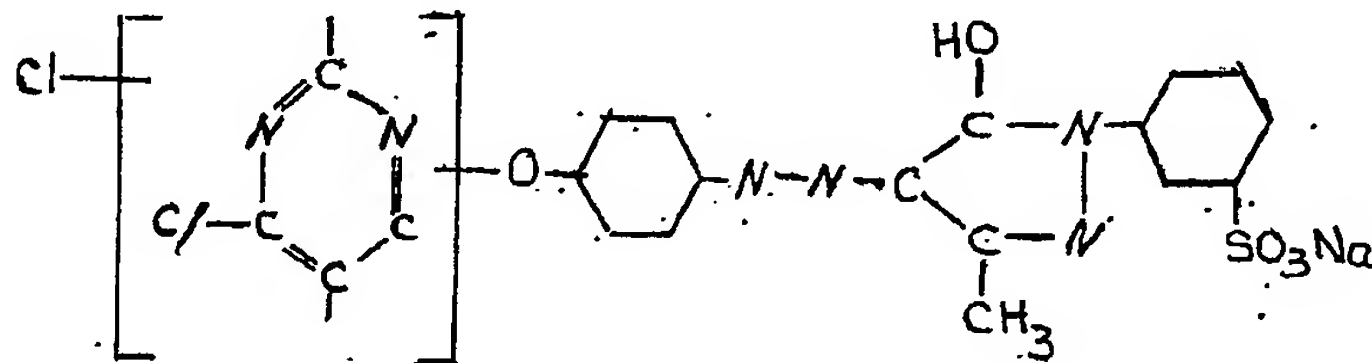
in the cyanuric ring in place of —NH—C<sub>2</sub>H<sub>4</sub>—OH a different group, e.g. —N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub> or



## EXAMPLE 5.

25

Mercerised cotton fabric is padded at room temperature with a solution of 1 part of the monoazo dye of the formula



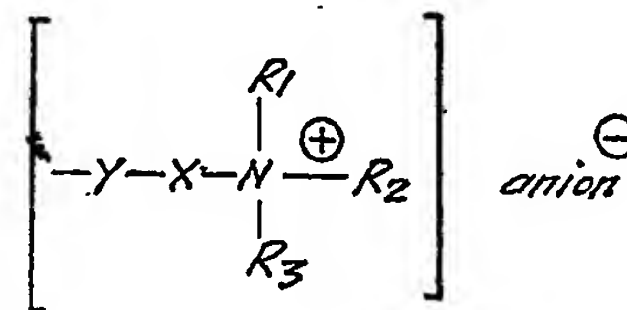
per 100 parts of water, and expressed so as to contain 70% of its weight of the liquor. The padding is fixed on a roller vat by treatment for 30 seconds at 40° in a solution having a pH of 12.25 and containing 200 g/l calcined sodium sulphate, 40 g/l sodium metasilicate and 20 g/l asymmetrical dimethylhydrazine, and is then rinsed in cold and warm water, soaped for 10 minutes at 100°, rinsed again and dried. A greenish yellow dyeing is obtained which is fast to light and wet treatments.

## WHAT WE CLAIM IS:—

1. A process for the dyeing and printing of cellulosic textile materials with reactive dyes, which are applied at 15—40°C and fixed at 15—40°C in an alkaline medium, which process consists in the use of a reactive dye of moderate substantivity as hereinbefore defined which contains a dichloropyrimidyl-5-carbonyl-group of the formula

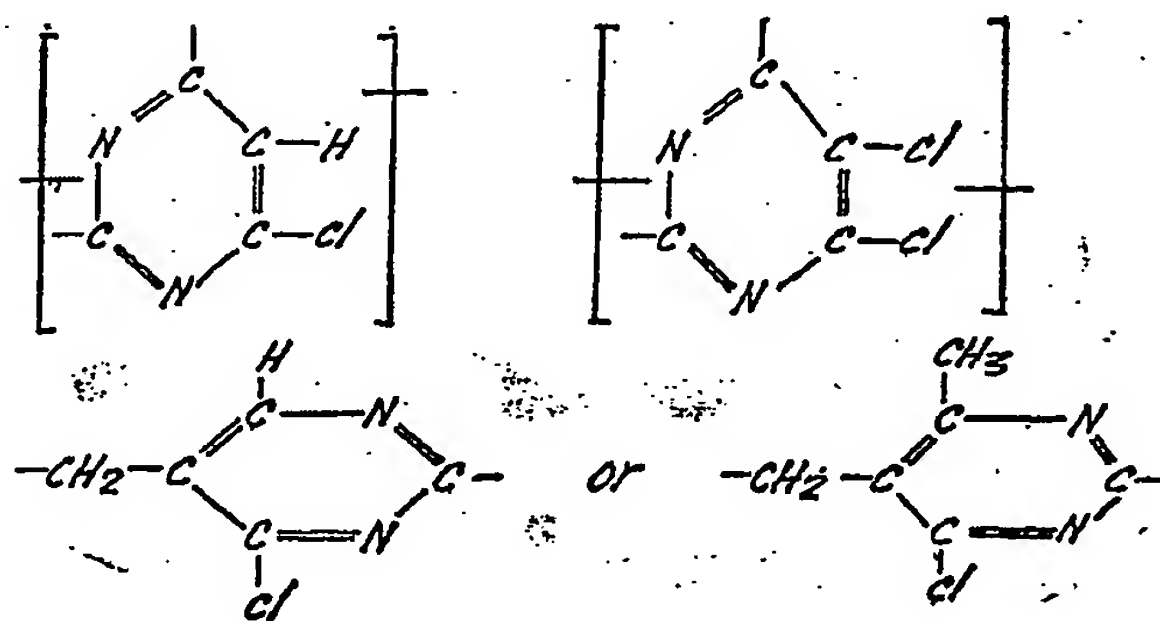


or a radical of the formula

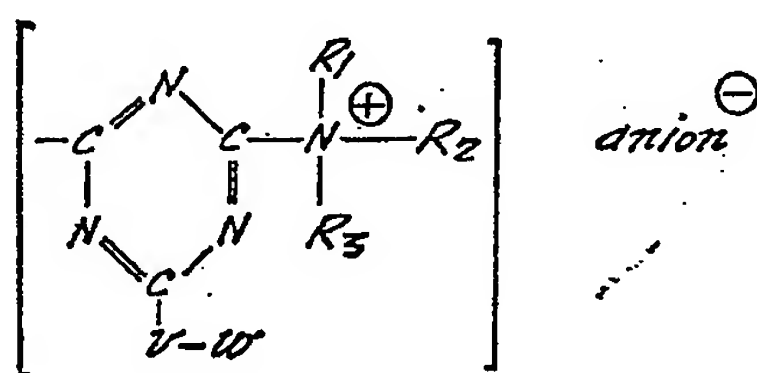


wherein X represents a halogen-substituted bridge member of the 1,3-diazine series, e.g.





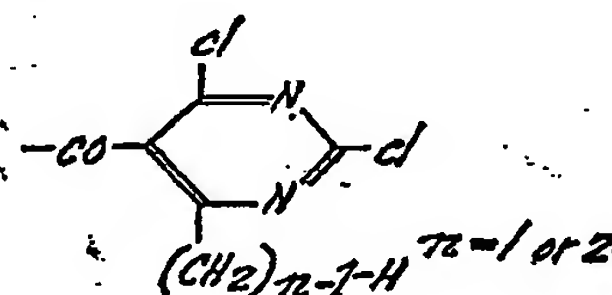
- Y represents an oxygen atom or an imino group, which may be alkylated,  
 $R_1$  represents  $-NH_2$ , and  
 5  $R_2$  and  $R_3$  each represent methyl or  $R_2$  and  $R_3$  together with N form a pyrrolidyl or piperidyl radical (when Y represents an oxygen atom the quaternation can be effected in the fixing bath itself) or  
 10 a radical of the formula



wherein

- V represents an oxygen or sulphur atom or a substituted or unsubstituted imino group,  
 15 W represents hydrogen or a substituted or unsubstituted alkyl, aralkyl, cycloalkyl or aryl radical and  
 $R_1$  and  $R_2$  and  $R_3$  have the meanings ascribed to them above, being a reactive dye whose constant of hydrolysis rate at the fixing temperature and at a pH value of 10.5 is greater than  $5 \times 10^{-3}$  min. — and carrying out the fixation in the pH range of from 8 to 14.  
 20 2. A process according to Claim 1 wherein the fixation is carried out without intermediate drying.  
 25 3. A process according to Claim 1, wherein the fixation is carried out with intermediate drying.  
 30 4. A process according to any of Claims 1 to 3, wherein the fixation is carried out during 5 to 60 seconds.  
 35 5. A process according to Claim 4, wherein the fixation is carried out during 5 to 10 seconds.  
 6. A process according to any one of claims 1 to 5, wherein the fixation is carried out in the pH range of from 8.5 to 12.5.

7. A process according to any of Claims 1 to 6, wherein a dye containing a dichloropyrimidyl-5-carbonyl-group of the formula 40

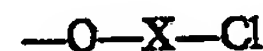


is used and wherein a fixation catalyst of the formula

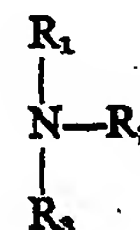


is employed, wherein

- $R_4$  represents methyl or  $-NH_2$ ,  
 $R_5$  and  $R_6$  each represent methyl or  $R_5$  and  $R_6$  together with N form a pyrrolidyl or piperidyl radical,  
 50 or  $R_5$ ,  $R_6$  and  $R_6$  together with N form the radical of triethylenediamine.  
 8. A process according to Claim 1, wherein a dye containing a radical of the formula 55



is used and the quaternisation is effected in the fixation bath itself with a compound of the formula



wherein X,  $R_1$ ,  $R_2$  and  $R_3$  have the meanings ascribed to them in Claim 1. 60

9. A process for the dyeing and printing of cellulosic textile materials with reactive dyes substantially as herein described and as illustrated in any of Examples 1 to 5.
- 5 10. Filaments, loose fibres or woven or knitted fabrics of natural cellulose, e.g. of cotton, mercerised cotton or linen, or of regenerated cellulose, e.g. viscose filament or staple fibre, cuprammonium rayon, or blended yarns
- 10 or fabrics or other articles composed of one of the aforementioned fibres and a natural or synthetic polyamide fibre, e.g. wool, silk, nylon, or a polyester or acrylic fibre which have been dyed or printed according to a process claimed in any one of Claims 1 to 9. 15

MEWBURN ELLIS & CO.,  
Chartered Patent Agents,  
70/72, Chancery Lane,  
London, W.C.2,  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.  
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which  
copies may be obtained.